

# Reducing 1,3-Dichloropropene Emissions from Soil Columns Amended with Thiourea

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Soil fumigants are becoming an important source of volatile organic compounds (VOCs) in air, especially in some agricultural areas. In this study, we used thiourea to construct a reactive surface barrier (RSB) at the soil surface for reducing 1,3-dichloropropene (1,3-D) volatilization. The agrochemical thiourea could rapidly transform volatile 1,3-D to nonvolatile products via an  $S_N2$  nucleophilic substitution reaction. A catalytic mechanism in thiourea-amended soil facilitated the conversion process. A packed soil column system was employed to investigate the emissions and distribution of 1,3-D and optimize the original fumigant emission-reduction strategy. Volatilization of 1,3-D from the soil surface was significantly reduced in columns amended with a thiourea RSB compared with that of bare soil. Volatilization flux and cumulative emissions decreased with increasing thiourea application rate and increasing fumigation depth in packed soil columns. Surface amendment with the RSB did not affect the subsurface distribution of 1,3-D in the soil profile. Combined application of a thiourea RSB and plastic tarps had a synergetic effect in emission control and could eliminate the relatively high fumigant flux that occurs upon tarp disruption. Therefore, this reduced-risk practice was very effective in reducing atmospheric emissions of VOCs from soil treatment with halogenated fumigants.

## Introduction

Fumigation has been used extensively for decades to control soilborne pests prior to crop planting. Due to the high volatility of fumigants, the primary environmental concern associated with the use of these pesticides is the emission of toxic volatile organic compounds (VOCs) into air (1–4). The occurrence of fumigants and their transformation products in the atmosphere can have a variety of harmful environmental effects. At high levels of exposure, these chemicals are a direct toxicological threat to public health. Farmers, farm workers, and residents living near areas in which pesticides are applied have greater risk of exposure to

these toxic chemicals (2, 5), since volatilization of fumigants is inevitable in field plots (6–8).

In addition to the direct effects of VOCs on environmental and human health, the United States Environmental Protection Agency (USEPA) and state air quality boards throughout the United States are concerned about the contribution of VOCs to the formation of tropospheric ozone. Ground-level ozone is a major component of photochemical smog in urban and rural areas. Generally, VOCs in combination with nitrogen oxides ( $NO_x$ ) are responsible for the occurrence of ground-level ozone in the presence of sunlight (9). Therefore, VOCs are currently regulated as ozone precursors. Previous efforts to reduce ozone pollution primarily focused on the control of industrial and automotive sources of VOCs. Recently, soil fumigants are receiving increasing attention as VOC ozone precursors, because research has indicated that as much as 20–90% of the applied fumigant may be released into the atmosphere (3, 4, 6–8, 10). For example, the fumigant chloropicrin has been verified to form ozone in combination with  $NO_x$  and other organic species present in the atmosphere (11). The U.S. EPA has established a more stringent ozone standard that requires additional VOC reductions from all sources, including pesticides (12). The Department of Pesticide Regulation (DPR) of California estimates that approximately 50–60% of VOC emissions from pesticides are due to fumigants (12). Therefore, decreasing fumigant emissions should contribute to the reduction of ground-level ozone to improve air quality.

Currently, numerous soil fumigation practices are being developed to minimize the release of fumigants into the air. Tarping the soil surface with plastic is routinely used to impede fumigant volatilization. However, the high permeability of polyethylene film to fumigants causes ineffective control of fumigant emissions (13–16). Moreover, fumigants and their degradation products trapped under the covering are released into the atmosphere once the plastic tarp is removed because of subsequent field uses (17, 18). Incorporation of biosolids such as manure into soil can stimulate the activity of fumigant-degrading organisms and thereby accelerate fumigant biodegradation (19–21). However, the biotic degradation process often results in the formation of smaller and more labile volatile products (22), which may contribute to the VOC load to the atmosphere. Reactive surface barrier (RSB), a chemical remediation technology, has been proposed to reduce fumigant emissions through rapid abiotic transformation of fumigants to nonvolatile products at the soil surface (23, 24). This approach has shown promise in preliminary experiments (24), but further research is required to investigate the effect of various application parameters on the control of fumigant emissions.

The primary objective of this study is to determine the effect of a thiourea RSB on the volatilization of the fumigant 1,3-dichloropropene (1,3-D) from soil columns under controlled conditions. Soil column experiments have been successfully used to monitor the emission and distribution of fumigants and to provide insight into fumigant behavior for a variety of fumigation practices (16, 25, 26). Soil column experiments provide a relatively rapid, convenient, and inexpensive method to screen and assess new fumigation methods, such as RSB, prior to their field evaluation.

## Experimental Section

**Materials.** The soil used in this study, an Arlington sandy loam (coarse-loamy, mixed, thermic Haplic Durixeralf), was collected from the University of California, Riverside Agricultural Experiment Station. Fresh soils were sampled from

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the top 15 cm of a field that has no history of fumigant application. Fresh soil was passed through a 2.0-mm sieve without air-drying and stored at 4 °C until use. The soil had a pH of 7.2 and organic carbon content of 0.92%.

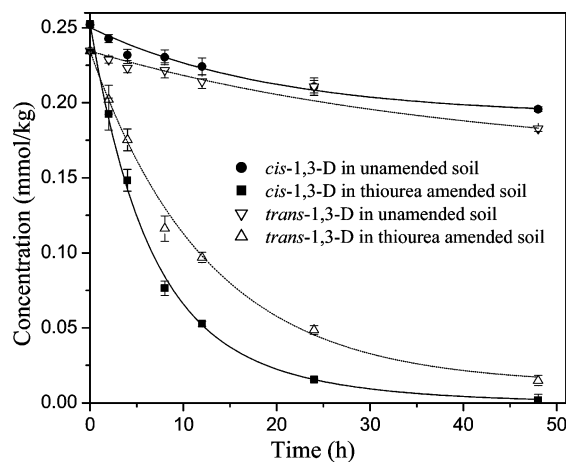
1,3-Dichloropropene standard (50.5% *cis* and 46.9% *trans* isomer) was donated by Dow AgroSciences LLC (Indianapolis, IN). Thiourea (99% purity) was purchased from Aldrich Chemical Co. (Milwaukee, WI). All chemicals were used as received.

**Batch Incubation Experiments.** Incubation experiments were conducted to determine the rate of 1,3-D dissipation in thiourea-amended and unamended soil. First, thiourea stock solution was added to Arlington sandy loam and thoroughly mixed in a plastic bag. Ten grams (dry weight equivalent) of the amended soil was weighed into 21-mL headspace vials and spiked with 1,3-D solution. This yielded soil samples with 4.0 mmol/kg thiourea, 0.5 mmol/kg 1,3-D, and a soil moisture of 10% (w/w). Unamended soil samples were prepared using similar procedures with no thiourea added. After spiking, all vials were capped immediately with Teflon-faced butyl rubber septa and incubated in the dark at  $21.0 \pm 0.5$  °C. Triplicate samples vials were sacrificed periodically by transferring them from the incubator to the freezer. All samples were frozen at -21 °C for 3 h. To extract 1,3-D residues from soil, the frozen sample vials were decapped, and ethyl acetate (10.0 mL) and anhydrous sodium sulfate (8.0 g) were added, followed by immediate recapping. The samples were vigorously shaken for 2 h and vortexed for 2 min at room temperature. An aliquot of each ethyl acetate extract was transferred to a GC vial and stored at -21 °C until the end of the experiment. Recovery experiments showed 1,3-D extraction efficiencies of 95% to 105% using this procedure.

Extracts were analyzed using a Hewlett-Packard (HP) 6890 GC equipped with an on-column injector, a microelectron capture detector ( $\mu$ ECD), and a 30 m DB-VRX, 0.25 mm i.d.  $\times$  1.4  $\mu$ m film thickness fused-silica capillary column (J&W, Folsom, CA). The GC conditions were 1.4 mL min<sup>-1</sup> carrier gas flow rate (He), 240 °C inlet temperature, and 290 °C detector temperature. The initial oven temperature was 50 °C for 1 min; the temperature was increased to 80 °C at 5.0 °C/min and held for 2.5 min, and then increased to 120 °C at 25 °C/min and held for 1 min. Under these conditions, the retention times for *cis*-1,3-D and *trans*-1,3-D were 8.0 and 8.9 min, respectively.

**Soil Column Experiments.** The column system utilized in the study was described in detail by Gan and co-workers (25, 26). Briefly, stainless steel columns (70 cm with 12 cm i.d.) were uniformly packed with fresh soil at a bulk density of 1.50 g cm<sup>-3</sup> and moisture of 5.4% (w/w). The top 5 cm of soil was amended with thiourea to construct an RSB within the column. Ports installed in the side wall of each column allowed the introduction of fumigant to the subsurface at various depths and the withdrawal of soil gas samples to monitor subsurface fumigant concentrations. A sampling chamber (4 cm with 12 cm i.d.) with an inlet and an outlet was sealed onto the top of soil column. A continuous and constant air flow (100 mL min<sup>-1</sup>) was passed through the sampling chamber to sweep fumigant vapor escaping from the soil surface into the headspace inlet of GC, which was directly connected to the outlet of the sampling chamber. Once 1,3-D was injected into the soil column at the depth of interest, fumigant volatilization flux from each column was automatically monitored at 42-min intervals using a computerized relay system in tandem with an HP 6890N GC.

The cumulative volatilization loss of the fumigant was calculated by integrating the instantaneous volatilization fluxes over the time for the entire experiment (14 days). Volatilization fluxes were calculated as mg min<sup>-1</sup> m<sup>-2</sup> and cumulative emission losses as a percentage of total applied



**FIGURE 1.** Dissipation of 1,3-D (0.5 mmol/kg) in unamended soil and soil amended with thiourea at 4.0 mmol/kg at  $21 \pm 0.5$  °C. The error bars represent the standard deviation of triplicate samples.

fumigant. The GC conditions used for on-line monitoring were as follows: 100- $\mu$ L gas sampling loop; 60 m DB-624, 0.25 mm i.d.  $\times$  1.4  $\mu$ m film thickness fused-silica capillary column (J&W, Folsom, CA); 1.5 mL min<sup>-1</sup> carrier gas flow rate (He); 100 °C isothermal oven temperature; 220 °C inlet temperature; 290 °C detector temperature. Under these conditions, the retention times for *cis*-1,3-D and *trans*-1,3-D were 7.0 and 8.0 min, respectively.

Three sets of column experiments were conducted to investigate the effect of RSB and 1,3-D application variables on 1,3-D emissions from soil. The first experiment was conducted using different thiourea amendment rates. Thiourea was mixed into the top 5 cm of soil, and 1,3-D (127  $\mu$ L) was injected at the center of the column 30 cm below the soil surface. The ratios of thiourea to 1,3-D were 0:1, 4:1, 8:1, and 20:1 (mol/mol), where 0:1 served as a control without thiourea addition. The second experiment was conducted by injecting 1,3-D (127  $\mu$ L) at 20, 30, and 40 cm depth. Volatilization flux and soil distribution of 1,3-D were measured in these columns both with a thiourea RSB (8:1 thiourea/1,3-D) and without surface amendment. The third experiment determined the 1,3-D volatilization loss from soil columns with a plastic tarp covering the thiourea RSB. Thiourea-amended soil (8:1) was used for the top 5 cm of soil in each column, and a high-density polyethylene (HDPE) (TriCal, Hollister, CA) or a virtually impermeable film (Hytibar, Klerk's Plastic Products, Richburg, SC) was installed above the RSB; thus, the fumigant had to diffuse through the thiourea RSB and the plastic film to enter the sampling chamber. 1,3-D (127  $\mu$ L) was injected at 30 cm depth. The plastic film was torn after 8 days to simulate tarp removal following soil fumigation. Duplicate columns were used for each treatment described above to quantify system variability.

To monitor the distribution of 1,3-D in the second experiment, gastight syringes were used to withdraw 0.1-mL aliquots of soil air from sampling ports located 2, 5, 10, 20, 30, 40, 50, 60, and 70 cm below the soil surface. Air samples were immediately transferred to 10-mL headspace vials. The concentration of 1,3-D in each vial was determined using an HP 6890 GC equipped with an automated headspace sampler (Agilent Technologies, Wilmington, DE). The operating conditions of the headspace sampler were set as follows: 80 °C oven temperature, 90 °C loop temperature, 100 °C transfer line temperature, 5-min vial equilibration time, and 0.2-mL sample loop; GC conditions were similar to those used for the batch incubation experiments.

## Results and Discussion

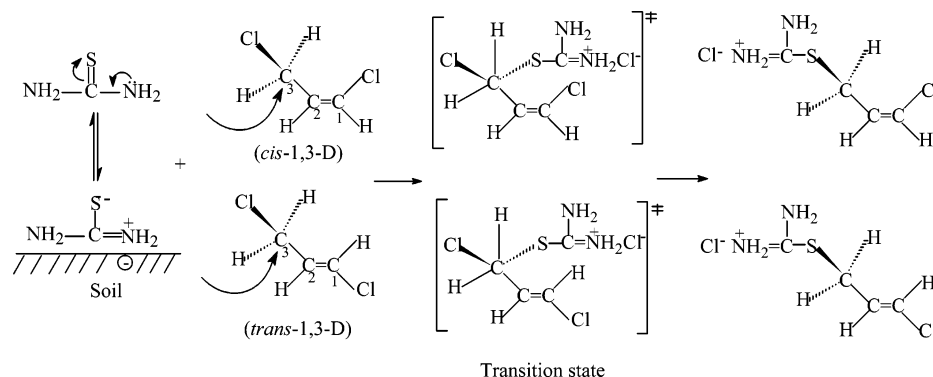
**Transformation of 1,3-D in Soil Amended with Thiourea.** Batch incubation studies indicated that 1,3-D dissipation

**TABLE 1. Second-Order Transformation Kinetics of 1,3-D in Thiourea-Amended Soil and Pseudo-First-Order Degradation Kinetics of 1,3-D in Unamended Soil**

	reaction coefficient			degradation coefficient		
	$k_2'$ (mmol/kg) <sup>-1</sup> h <sup>-1</sup>	DT <sub>50</sub> (h) <sup>a</sup>	$r^2$	$k'$ (h) <sup>-1</sup>	$t_{1/2}$ (h)	$r^2$
<i>cis</i> -1,3-D	$2.70 (\pm 0.04) \times 10^{-2}$	6.5	0.992	$4.60 (\pm 0.50) \times 10^{-3}$	150.6	0.828
<i>trans</i> -1,3-D	$1.48 (\pm 0.06) \times 10^{-2}$	11.9	0.988	$4.74 (\pm 0.39) \times 10^{-3}$	146.2	0.882

<sup>a</sup> DT<sub>50</sub> represents the 50% disappearance time of 1,3-D in amended soil and was obtained from eq 4 where  $C = C_0/2$ .

## SCHEME 1



was accelerated in soil amended with thiourea compared to unamended soil (Figure 1). The rate of transformation of 1,3-D in thiourea-amended soil may be expressed as

$$-dC/dt = k_{\text{obs}}C^a = k_2C^aX^b + k'C \quad (1)$$

where  $k_{\text{obs}}$  is the observed rate constant,  $k_2$  is the reaction rate constant of 1,3-D and thiourea, and  $k'$  is 1,3-D degradation rate constant in soil;  $C = [1,3\text{-D}]$ ,  $X = [\text{thiourea}]$ ;  $a$  and  $b$  represent the order of reaction with respect to 1,3-D concentration ( $C$ ) and thiourea concentration ( $X$ ) in question, respectively. If considering the reaction order  $a$  and  $b = 1$ , eq 1 becomes

$$-dC/dt = k_0C = k_2'CX + k'C \quad (2)$$

The transformation of 1,3-D in thiourea-amended soil is much faster than 1,3-D degradation in unamended soil (Figure 1), so eq 2 may be simplified to a second-order reaction

$$-dC/dt = k_0C \approx k_2'CX = k_2'C(C - C_0 + X_0) \quad (3)$$

where  $k_0$  represents the overall pseudo-first-order rate constant,  $k_2'$  is the second-order reaction rate constant between 1,3-D and thiourea, and  $C_0$  and  $X_0$  are the initial concentration of 1,3-D and thiourea, respectively. Upon rearrangement and integration, a solution of eq 3 is obtained

$$C = C_0 \frac{(X_0 - C_0) \exp[-k_2'(X_0 - C_0)t]}{X_0 - C_0 \exp[-k_2'(X_0 - C_0)t]} \quad (4)$$

The second-order rate constant ( $k_2'$ ) can be computed from least-squares fit of the experimental data (1,3-D concentration with time) to eq 4 (Table 1). Pseudo-first-order kinetics is usually used to approximate the degradation of pesticides in unamended soil (27).

Under these experimental conditions, the 50% disappearance time (DT<sub>50</sub>) of both 1,3-D isomers in thiourea-amended soil was significantly decreased compared to their degradation half-life ( $t_{1/2}$ ) in unamended soil. The DT<sub>50</sub> values of *cis*-1,3-D and *trans*-1,3-D were approximately 23 and 12 times below that of their  $t_{1/2}$  in soil, respectively (Table 1).

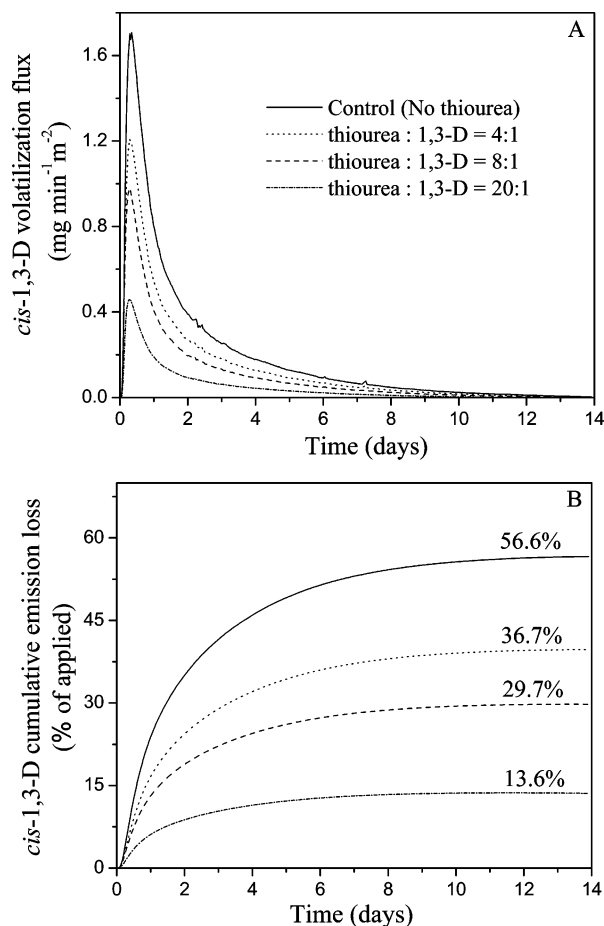
These results clearly indicate that enhanced dissipation of 1,3-D is obtained in amended soil due to reaction with thiourea.

**Mechanism of Enhanced 1,3-D Dissipation in Amended Soil.** Thiourea as a nucleophile may react with halogenated compounds via an S<sub>N</sub>2 nucleophilic substitution process (28). The reaction occurs by displacement of the halide ion to yield an alkylisothiourethane salt. As in the reaction of methyl iodide (23) and chloroacetanilide herbicides (29) with thiourea in soil, the potential negative charge at the soil surface may facilitate the stability of the resonance structure of thiourea (Scheme 1), favoring electron transfer from the amino group rendering the thiono group as a stronger nucleophile. The nucleophilic center (sulfur) of thiourea may readily attack 1,3-D to liberate a chloride at C3, yielding a nonvolatile chloropropene-substituted isothiourethane salt (Scheme 1). This transformation product, which has been identified in earlier results, may undergo further transformation under alkaline conditions (24). Similar S<sub>N</sub>2 substitution reactions have also been reported for reaction of 1,3-D with metam sodium (30).

The 1,3-D investigated in these experiments is a mixture of *cis* and *trans* isomers. The *cis* isomer degrades more quickly than the *trans* isomer of 1,3-D (Figure 1 and Table 1). This may be due to the C1 chlorine hindering C2–C3 bond rotation in the transition state of the *cis* form (Scheme 1), which destabilizes its transition state relative to that of the *trans* isomer.

**Effect of Thiourea Application Rate on 1,3-D Emission.** The maximum flux of *cis*-1,3-D and *trans*-1,3-D from the control soil column (no thiourea RSB) were approximately 1.7 mg min<sup>-1</sup> m<sup>-2</sup> and 1.0 mg min<sup>-1</sup> m<sup>-2</sup> and occurred approximately 7 and 12 h after fumigant application at a depth of 30 cm (Figure 2A and Figure S-1A in the Supporting Information). The construction of a thiourea RSB in the top 5 cm of the soil column substantially reduced 1,3-D volatilization flux into air throughout the experimental period (Figures 2A and S-1A). The volatilization flux decreased with increasing thiourea amendment rate (Figures 2A and S-1A). For example, the maximum volatilization flux of *cis*-1,3-D was approximately 0.5 mg min<sup>-1</sup> m<sup>-2</sup> when the application ratio of thiourea/1,3-D was 20:1 (Figure 2A), a greater than 3-fold decrease relative to that of no RSB. Similar decreases



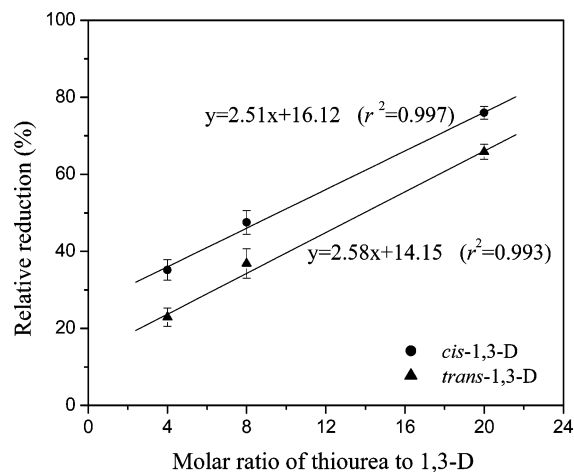


**FIGURE 2.** Volatilization of *cis*-1,3-D from soil columns with different rates of thiourea amendment: (A) instantaneous flux; (B) cumulative volatilization. The fumigant was injected at 30 cm depth.

in *trans*-1,3-D volatilization flux were also observed (Figure S-1A).

The cumulative emissions losses of *cis*-1,3-D and *trans*-1,3-D were 56.6% and 51.0% for the control column (no RSB) with most of the fumigant loss occurring within the first 6 days (Figures 2B and S-1B). The high volatilization loss of 1,3-D indicates some strategies for reducing fumigant emissions should be required to aid in reducing VOC concentrations and acute exposure potentials. Application of thiourea at the soil surface significantly reduced 1,3-D loss through volatilization. Cumulative volatilization loss decreased with increasing thiourea application rate (Figures 2B and S-1B). For example, the cumulative losses of *cis*-1,3-D from RSB-treated soil columns were 36.7%, 29.7%, and 13.6%, respectively, at application ratios of thiourea/1,3-D of 4:1, 8:1, and 20:1 (Figure 2B).

A quantitative effect of thiourea application rate on 1,3-D emission reduction is illustrated by comparing the relative difference in cumulative emissions in thiourea-amended columns and control soil columns. The relative reduction in cumulative emissions of both isomers was linearly correlated with the thiourea/1,3-D mol ratio (Figure 3). Here, the emission loss of 1,3-D from the unamended soil column is defined as 100%. The strong correlation (Figure 3) suggests that 1,3-D emissions are dependent on the thiourea application rate in the soil columns. The relative emission loss of both 1,3-D isomers decreased approximately 2.5% to ~2.6% with each unit increased in the thiourea/1,3-D mol ratio. The dependence of fumigant emissions on the thiourea application rate indicates that the effectiveness of a thiourea RSB in controlling 1,3-D volatilization is a function of the amount of thiourea present at the soil surface.



**FIGURE 3.** Effect of thiourea application rate on the relative reduction of 1,3-D emission loss. The fumigation depth was 30 cm below the soil column surface.

**Effect of Application Depth on 1,3-D Emissions from Soil with a Thiourea RSB.** The cumulative losses of 1,3-D over 14 days are summarized in Table 2 for both unamended and RSB-amended soil columns. Cumulative 1,3-D emissions consistently decreased with increasing depth of 1,3-D application (Table 2), in agreement with previous studies indicating that deep injection reduces fumigant volatilization (8, 16). Increasing the fumigant travel path length by increasing the depth of injection extends the residence time of the fumigant in soil, allowing for more extensive biotic and abiotic degradation.

Cumulative emissions of both 1,3-D isomers was substantially reduced in RSB-amended columns compared with those of the unamended columns at each fumigation depth (Table 2). A relative emission reduction of 1,3-D was calculated by comparing the difference of fumigant losses from thiourea-amended columns and control soil columns. The relative reduction in cumulative 1,3-D emissions was not statistically different for different fumigant application depths (Table 2), indicating that 1,3-D application depth did not affect the efficiency of the RSB in controlling 1,3-D emissions.

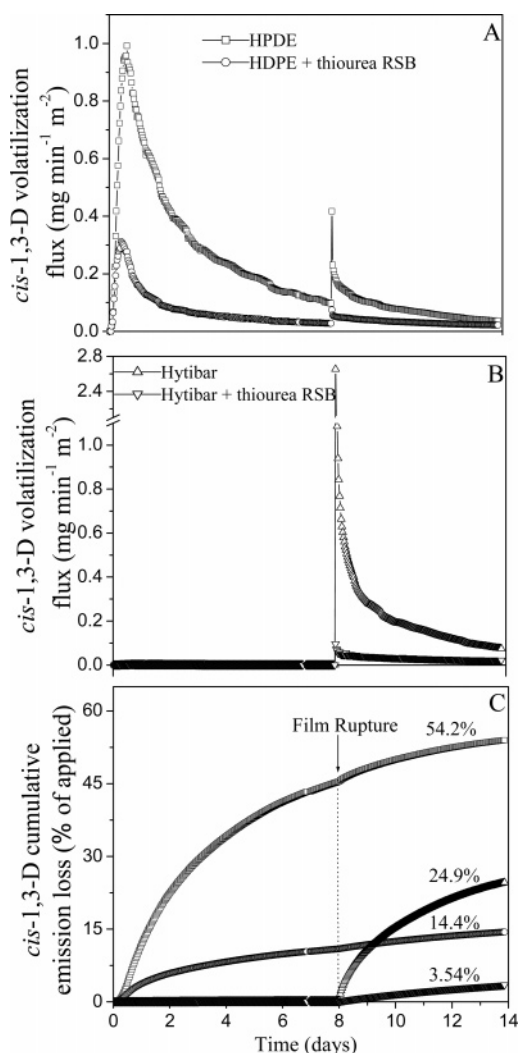
A successful fumigation requires a uniform distribution of fumigant in the targeted soil profile. The concentration of 1,3-D in the soil air was monitored with time throughout the 70 cm soil profile to compare the distribution of the fumigant in soil columns with and without a thiourea RSB. Similar distribution patterns of *cis*-1,3-D were observed in soil columns with and without a thiourea RSB following fumigation at 20 cm depth (Figure S-2 in the Supporting Information), with the only exception occurring at 2 cm (within the 5 cm deep RSB). A similar result was also obtained for *trans*-1,3-D. It suggests that the thiourea RSB does not influence the subsurface distribution of 1,3-D. The application of a thiourea RSB may be considered chemically analogous to a physical barrier such as a plastic film in effectively reducing fumigant volatilization. Moreover, this approach may have additional benefits for the protection of air quality because the reaction between 1,3-D and thiourea produces nonvolatile transformation products that will not contribute toxic volatile contaminants to air or potentially participate in ozone formation reactions.

**Integration of RSB Application with Conventional Plastic Tarps.** Use of polyethylene or other plastic films as soil covers is part of current conventional soil fumigation practices. In comparison with uncovered soil (Figures 2 and S-1), covering the soil surface with a commercial polyethylene (HDPE) film significantly delayed 1,3-D volatilization and decreased the

**TABLE 2. Effect of Fumigation Depth on Cumulative Emission Loss of 1,3-D over 14 Days from Soil Columns with and without Surface Amendment of Thiourea**

treatment	total emission of 1,3-D (% of applied)					
	unamended soil column		soil column amended with thiourea (mol ratio of thiourea/1,3-D = 8:1)		relative reduction (%)	
	<i>cis</i>	<i>trans</i>	<i>cis</i>	<i>trans</i>	<i>cis</i> <sup>a</sup>	<i>trans</i> <sup>a</sup>
20 cm	67.3 ± 6.4	64.0 ± 7.1	32.3 ± 3.5	40.5 ± 3.9	52.0 ± 11.9	36.7 ± 13.3
30 cm	56.6 ± 5.4	51.0 ± 5.8	29.7 ± 2.6	32.2 ± 3.5	47.5 ± 11.3	36.8 ± 13.1
40 cm	50.5 ± 3.7	42.5 ± 4.5	27.8 ± 0.5	28.4 ± 1.2	45.1 ± 8.0	33.1 ± 15.2

<sup>a</sup> Nonsignificant between different fumigation depths at  $p \leq 0.05$  using a *t* test.



**FIGURE 4. Volatilization flux of *cis*-1,3-D following injection at 30 cm depth from soil columns treated with a thiourea RSB and HDPE film (A) or Hytibar film (B), as well as their cumulative emission losses (C). Thiourea RSB indicates surface amendment with thiourea at 8:1 (thiourea/1,3-D mol ratio).**

volatilization flux of 1,3-D (Figure 4A and Figure S-3A in the Supporting Information). For example, for 1,3-D application at 30 cm depth, the maximum flux of *cis*-1,3-D from a HDPE-covered column occurred at ~18 h (Figure 4A) compared to ~7 h in an untarped column (Figure 2A), and the magnitude of the maximum flux of *cis*-1,3-D was reduced by about 40% in comparison with that of the uncovered column. Although the maximum flux of 1,3-D was decreased using HDPE alone, fumigant volatilization continued at a relatively high level for several days (Figures 4A and S-3A). Thus, the cumulative loss of both 1,3-D isomers was only slightly reduced (<10%

decrease) using HDPE (Figures 4C and S-3C). These results suggest that the use of HDPE tarps may help to reduce the acute exposure of farmers and farm workers, but chronic exposures may remain of similar magnitude. Hytibar is a low-permeability plastic film that has been demonstrated to have great potential for controlling fumigant emissions (18). In these experiments, covering the soil surface with Hytibar effectively contained fumigant vapors in the soil and resulted in extremely low volatilization of 1,3-D while the film remained intact (Figures 4B and S-3B). In comparison to HDPE film, the cost of Hytibar film is more expensive, but it may provide better fumigant containment and greater pest control efficacy with minimal adverse environmental effect.

After 8 days, the HDPE and Hytibar films were torn to simulate tarp removal, which is required prior to crop planting. An immediate flush of 1,3-D occurred following the tear which decreased gradually (Figures 4 and S-3). For the Hytibar-covered soil, in which fumigant vapors were more effectively trapped below the impermeable tarp, volatilization flux increased drastically upon tarp removal, from about 0.01 to >2.7 mg min<sup>-1</sup> m<sup>-2</sup> (Figures 4B and S-3B). Cumulative emissions of 1,3-D from Hytibar-tarped soil were 24.9% for *cis*-1,3-D and 20.2% for *trans*-1,3-D, most of which occurred following tarp removal (Figures 4C and S-3C). These results suggest that tarp removal provides the potential for increased acute fumigant exposure, and virtually impermeable films used alone may be inadequate for reducing volatilization of fumigants unless the tarp remains intact for extended periods.

Covering the soil surface with both a plastic film and a thiourea RSB resulted in a substantial reduction in emission losses (Figures 4 and S-3). Increased containment provided by the plastic film afforded more time for 1,3-D transformation within the RSB. Much lower 1,3-D volatilization flux was observed following film rupture from the RSB soil column. Moreover, using both Hytibar and a thiourea RSB, cumulative 1,3-D volatilization losses were only 3.5% and 5.5% for *cis*- and *trans*-1,3-D; cumulative emissions were decreased primarily through the reduction in flux following tarp removal (Figures 4 and S-3). Similarly, combined application of HDPE and thiourea at the soil surface significantly reduced the volatilization flux and cumulative loss of 1,3-D, although to a lesser extent than for the virtually impermeable Hytibar film. Cumulative 1,3-D emissions from soil columns covered with both HDPE and a thiourea RSB were less than half that from columns tarped with HDPE only. Additionally, the combined application of HDPE and thiourea RSB resulted in lower emissions than when only an 8:1 thiourea RSB was used (Figure 2).

The results of these experiments indicate that a thiourea RSB may be at least as effective in controlling emissions as a plastic tarp removed after 8 days under laboratory conditions. Adoption of the RSB technique may have the added benefit of reducing ozone formation reactions in the atmosphere since the transformation products are nonvolatile. Integrating impermeable plastic tarps with RSB technology may provide opportunities for optimized fumigant pest

control efficacy with minimal fumigant emissions to the atmosphere. Additional research is required to observe potential effectiveness of RSB in controlling fumigant emissions under field conditions, to compare the economics for various mitigation strategies, and to develop a feasible management practice that allows the continued use of soil fumigants in agriculture while minimizing human exposure and VOC concentrations near the soil/air interface.

### Supporting Information Available

Two figures showing volatilization of *trans*-1,3-D from soil columns with different thiourea amendment rates (Figure S1) and with integrated application of RSB and plastic films (Figure S3); one figure showing distribution of *cis*-1,3-D in the soil columns (Figure S2). This information is available free of charge via the Internet at <http://pubs.acs.org>.

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